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## **TECHNICAL NOTE No. 5**

### **SPECTROSCOPIC STUDIES: PART 2, THE INFRA-RED SPECTRA AND STRUCTURE OF METHOXYACETONITRILE AND METHYL-CHLOROMETHYLETHER**

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*List of Technical Notes*

TN-1 : Force Constants in Boron Trihalides. June, 1963.

TN-2 : Infra-red Dispersion Studies : Part I, Dichloro-, Dibromo-, and Diiodomethane.  
June, 1963.

TN-3 : Vibrational Frequencies and Electronegativities. June, 1963.

TN-4 : Spectroscopic Studies : Part I, The Infra-red Spectrum and Structure of Sodium Nitromethane.

TN-5 : Spectroscopic Studies : Part 2, The Infra-red Spectra and Structure of Methoxyacetonitrile  
and Methyl-Chloromethylether.

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## TECHNICAL NOTE No. 5

### SPECTROSCOPIC STUDIES: PART 2, THE INFRA-RED SPECTRA AND STRUCTURE OF METHOXYACETONITRILE AND METHYL-CHLOROMETHYLETHER

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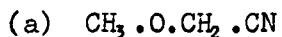
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The infra-red spectra of methoxyacetonitrile and methyl-chloromethyl-ether have been studied in solution and in the vapour and liquid states.

In the vapour state the band contours prove that the molecules are most stable when they have a slightly twisted trans conformation.

Methoxyacetonitrile (a) and methyl- chloro- methyl-ether (b) differ only in that the nitrile group of one is replaced by a chlorine atom.



Since the nitrile group and the chlorine atom have approximately the same electronegativity and mass it is reasonable to expect that the vibrational frequencies of the  $\text{CH}_3\text{.O.CH}_2\text{-}$  group will change but little in going from (a) to (b).

In both molecules rotation about the  $(\text{CH}_3)\text{O} — \text{C(H}_2\text{X)}$  bond is possible. (Fig. 3.) In their most stable states the molecules will have particular conformations corresponding to certain definite values for the moments of inertia. A study of the band contours, obtained from vapour phase spectra, then, should give a reliable indication as to the most stable conformation.

Methyl chloromethyl ether, together with the corresponding thio-ether, has been studied by Hayashi.<sup>2</sup> The Raman spectra of (a) and (b) have been recorded.<sup>2,3</sup>

EXPERIMENTAL.

Methoxyacetonitrile was prepared by addition of excess dimethyl sulphate to the product of reaction between potassium cyanide and formalin solution at temperatures below 10°C. The oily liquid with a pyridine-like smell was extracted with ether. The ether layer was dried, the ether removed and the residue distilled at atmospheric pressure. The observed boiling point was 121°C. (Literature<sup>4</sup> 119°C at 736 m.m.).

Methyl-chloromethyl-ether was prepared by the reaction between methanol formalin and hydrogen chloride, as described by Marvel and Porter<sup>5</sup>. The observed boiling point was 53.5°C at atmospheric pressure, to be compared with 55-60°C reported by Marvel and Porter.

The spectra were recorded on a Grubb Parsons G.S. 2A double beam infrared spectrometer calibrated with ammonia gas.

A pyrex glass vapour cell which allowed a temperature variation over the range 20°C to 200°C was used to record the vapour spectra. Matched metal cells (4.72m.m. and 9.78m.m. in length) were used to record solution spectra in chloroform, carbon tetrachloride and carbon disulphide solvents. The spectra of capillary and 0.1 m.m. thick, liquid films were also obtained.

The spectra are reproduced in figs. 1 and 2 and the frequencies given in tables 1 and 2.

The Stable Conformations.

The type of contour obtained for vibrational bands (i.e. the PQR structure) and the P-R sub-band separation depend critically upon the moments of inertia of the molecule. These, in turn, depend upon the conformation of the mol-

ecule (fig. 3.) As one part of the molecule rotates with respect to the other the absolute and relative magnitudes of the three principal moments of inertia change continuously: consequently the band contours and separations also change.

Molecular dimensions have not been determined for methoxyacetonitrile or for methyl-chloromethylether. Hence, from a study of similar molecules the parameters given in table 3 were chosen. With these values moments of inertia were calculated for each of the conformations given in fig. 3. (see table 4.).

The moments of inertia indicate that the molecules approximate to symmetric rotors especially for conformations near to (V). Using the theory developed by Gerhard and Dennison the P-R separations have been calculated, for parallel type bands, from the expression,

$$\Delta \nu (P, R) = \frac{S}{\pi} \left( \frac{kT}{I} \right)^{1/2}$$

where  $S = \frac{0.721}{(J_1 + 4)^{1/2}}$ ,  $\beta = (I - I_A)/I_A$ ,

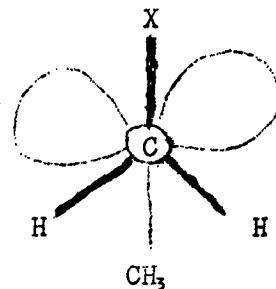
and  $I = (I_B + I_C)/2$ .

The values obtained are given in table 5, and expressed diagrammatically in fig. 4. The P-R separations found experimentally for parallel-type bands (or type A bands as described by Badger and Zumwalt<sup>7</sup>) are given in table 6.

From a comparison of the observed and calculated P-R separations it is

evident that, in both cases, the stable conformations are very close to model (V). That is the 'heavy' atom skeleton is almost planar-trans in form. This conclusion differs from that of Hayashi<sup>2</sup> who favours a gauche conformation fig. 3, II) for methyl chloromethyl-ether in the vapour state.

If the oxygen lone-pairs forming atomic dipoles are taken into account the terminal groups are seen to be staggered about the C-O bond.



In terms of bond-bond and bond-lone-pair repulsions this represents a most reasonable model.

Vibrational Assignment.

All the fundamental modes of vibration are infra-red active. The vibrations can be conveniently divided for discussion into two groups, viz. (i) the methyl and methylene vibrations, and (ii) those associated with the COCX skeleton.

(i) CH Vibrations.

Tables 1 and 2 contain the assignments for these molecules made on the basis of vapour phase band contours and comparisons with related molecules.

The ranges within which the various types of methyl vibrations occur are well-known and there is little uncertainty in the assignments made in tables 1 and 2.

The assignment of frequencies to the methylene bond-stretching modes is straightforward but this is not the case with the various deformation modes since they tend to vary over large spectral regions. For example the  $\text{CH}_2$ -rocking frequency occurring at  $1176 \text{ cm}^{-1}$  in  $\text{CH}_2\text{F}_2$  is found at  $714 \text{ cm}^{-1}$  in  $\text{CH}_2\text{I}_2$ , a decrease of some 39%.

In a recent study<sup>11</sup> relations have been found between the methylene deformation frequencies in  $\text{CH}_2\text{XY}$  molecules and the electronegativity product  $\chi(X)\chi(Y)$ . These correlations have been used to predict 'group electronegativities of 3.76(CH<sub>3</sub>.O) and 3.20(CN) corresponding to frequency values centred near to 1470, 1340, 1250 and 1,000  $\text{cm}^{-1}$  respectively for the bending, wagging, twisting, and rocking CH<sub>2</sub> vibrations. The observed values are in good accord with

these predictions (tables 1 and 2).

The vapour spectra of the compounds are not identical in the region between  $1,400 \text{ cm}^{-1}$ . and  $1,300 \text{ cm}^{-1}$ . Two absorption bands, one, weak, with an 'A, B' contour at  $1,397 \text{ cm}^{-1}$ . and the other, stronger in intensity with an almost perfect 'A' type contour at  $1324 \text{ cm}^{-1}$ , were observed in the spectrum of methyl chloromethylether. One complex band was observed in the spectrum of methoxyactonitrile centred at  $1364 \text{ cm}^{-1}$ . The difference between the two spectra is explicable in terms of Fermi resonance between the two vibrational modes (symmetric  $\text{CH}_3$  bending and wagging  $\text{CH}_2$ ) which belong to the same symmetry class. Evidence for this is the almost equal difference in frequency between these two absorption bands in (b) and the one complex band in (a).

(b) $\text{CH}_3\text{OCH}_2\text{Cl}$	1400	$36 \text{ cm.}^{-1}$
(a) $\text{CH}_3\text{OCH}_2\text{CN}$	1364	$40 \text{ cm.}^{-1}$
(b) $\text{CH}_3\text{OCH}_2\text{Cl}$	1324	

It is rather surprising that Fermi resonance is operative in (b) and not (a). The first overtone of the carbon-chlorine stretching vibration should occur close to  $1360 \text{ cm}^{-1}$ , in the vapour spectrum of (b) and the interaction of this binary transition with the superimposed fundamentals might be the factor that results in difference in the two spectra.

(ii) Skeletal vibrations.

Three bands are expected to arise from the skeletal stretching vibrations in methyl chloromethyl ether. Two of these are best regarded as an asymmetric and symmetric stretching mode of the COC grouping,  $\nu_a(\text{COC})$  and  $\nu_s(\text{COC})$  whilst the third,  $\nu(\text{CCl})$ , is primarily localized within the CCl bond. In methoxyacetonitrile there are four stretching modes,  $\nu_a(\text{COC})$ ,  $\nu_s(\text{COC})$ , and two others which can be approximately described as  $\nu(\text{CC})$  and  $\nu(\text{CN})$ .

The  $\nu(\text{CN})$  fundamental occurs near  $2250 \text{ cm}^{-1}$ , in all phases, with the very low intensity characteristic of  $\beta$ -oxygenated nitriles.

The assignment of the vibrations of the COCX chain in these molecules was facilitated by a direct comparison of the vapour spectra. Three absorption bands, of strong to medium intensity, were found in the region 1150 to  $800\text{cm}^{-1}$ , in the spectrum of methoxyacetonitrile. The strong absorption with an almost pure B type contour, at  $1132 \text{ cm}^{-1}$ , is assigned to the  $\nu_a(\text{COC})$  stretching vibration. The frequency of the carbon-oxygen stretching vibration in gaseous methanol is  $1030 \text{ cm}^{-1}$ . If it is assumed that the coupling between the symmetric and asymmetric modes of vibration of the COC chain results in a splitting of degenerate energy levels to give energy level pairs equally spaced on either side of the unperturbed  $\nu(\text{CO})$  vibrational level, it can be predicted that the frequency of the symmetric stretching vibration of the COC chain will be near

$$1030 - (1130 - 1030) = 930 \text{ cm.}^{-1}$$

Two absorption bands, with hybrid contours, at  $932 \text{ cm}^{-1}$ , and  $890 \text{ cm}^{-1}$ , were

observed in the vapour spectrum of methoxyacetonitrile. The higher frequency band is therefore assigned to  $\nu_s(\text{COC})$  and the other to  $\nu(\text{CC})$ . This assignment is supported by the fact that replacement of the nitrile group by chlorine results in the disappearance of the  $890 \text{ cm}^{-1}$ , band, but does not significantly perturb the spectrum above  $900 \text{ cm}^{-1}$ . This is to be expected because the chlorine atom does not differ much in mass or electronegativity from the nitrile group.

It has been shown that for molecules exhibiting rotational isomerism certain group frequencies are characteristic of particular isomeric conformations. For example in trans-monochlorinated hydrocarbons  $\nu(\text{CCl})$  varies from  $726(n\text{-propyl})$  to  $616^{-1}$ , in tert.amyl chloride, whilst the gauche frequencies range between  $645$  and  $560 \text{ cm}^{-1}$  for the same series.<sup>12</sup> In the spectrum of methyl chloromethyl ether only one  $\nu(\text{CCl})$  band centred at  $646 \text{ cm}^{-1}$  was detected. This comparatively high value underlines the correctness of choosing a trans-conformation. The absence of a second  $\nu(\text{CCl})$  band indicates that the gauche isomer is present to a very small extent, if at all.

The bond-bending fundamentals of the skeleton lie below the range studied. The vibrations can be approximately described for  $\text{CH}_3\text{OCH}_2\text{Cl}$  as COC bending -  $b(\text{COC})$ ,  $b(\text{OCCl})$ , both in the plane of the skeleton framework, and an out-of plane vibration which could be described as  $b(\text{OC})$  or  $b(\text{CCl})$ : for  $\text{CH}_3\text{OCH}_2\text{CN}$  one has  $b(\text{COC})$ ,  $b(\text{OCC})$ ,  $b(\text{CCN})$  all in-plane and either  $b(\text{OC})$  or  $b(\text{CN})$  out-of-plane.

The corresponding frequencies are expected to be below  $500 \text{ cm}^{-1}$  as is clearly shown by table 7.

Three weak bands at 838, 709, and 586 c.m.<sup>-1</sup> were observed in the spectrum of liquid methoxyacetonitrile. These can be assigned as overtone or combination bands in a number of ways. The interpretation of other combination bands observed in the higher frequency region is made more plausible if these frequencies are assigned as follows:-

$$\begin{aligned} b(COC) \sim b(OCC) &= 425 \text{ c.m.}^{-1} \\ b(CCN), \text{ in plane} &= 360 \text{ cm.}^{-1} \\ b(CCN), \text{ out of plane} &= 230 \text{ c.m.}^{-1} \end{aligned}$$

The torsional modes of methyl groups about a C-O bond have been assigned tentatively<sup>9</sup> to bands at 160 and 230 c.m.<sup>-1</sup>. The torsional mode



would therefore be expected to have an even lower frequency.

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TABLE 1: INFRARED SPECTRUM OF METHOXACETONITRILE

LIQUID (Raman)	Capillary 0.75mm	SOLUTIONS <chem>CCl4</chem> (0.5cm.)	VAPOUR <chem>CS2</chem> (0.5cm.)	ASSIGNMENT.
	14447			$3008+1450 = 4458$
	4404			$2946+1460 = 4406$
	4356			$3003+1370 = 4373$
	4269			$3008+1287 = 4295$
	4201			$3008+1196 = 4204$
	4064			$2916+1158 = 4074$
	3949			<del>2857</del> $+1115 = 3952$
	3640			$2256+1380 = 3636$
	3563			$2257+1289 = 3546$
	3132			$2257+886 = 3143$
3009			3018 {	$\text{CH}_2$ Asymmetric Stretch
2930			3010 }	$\text{CH}_2$
2946			3000 }	Symmetric Stretch
2933			2950 }	$\text{CH}_3$ Asymmetric Stretch
2914			2931 }	$\text{CH}_3$ Asymmetric Stretch
			2908 }	$\text{CH}_3$ Asymmetric Stretch
			2397 }	
			2389 }	
2872			2849	$2831 \}$
2832			2824	$2822 \}$
2627			2656	$1289+1370 = 2659$
			2629	$1460+1158 = 2618$
			2603	$1450+1158 = 2613$
			2464	$1289+1196 = 2485$
			2444	<del>1289+1158 = 2447</del>
			2389	<del>281196 = 2392</del>
			2302	<del>2x1158 = 2316</del>
			2256	CN Stretching
2243				2251

TABLE 1. (Cont.)

Liquid (Raman)	Capillary 0.75mm.	SOLUTIONS $\text{CCl}_4$ (0.5 cm) $\text{CS}_2$ (0.5 cm)	VAPOUR	ASSIGNMENT.
2207	2206		2136	$2x1115$ = 2230
2105	2105		2060	$1115+1014$ = 2129
2064	2061		2078	$886+1196$ = 2082
2023	2021		2025	$886+1158$ = 2044
1757	1758	1758	1760	$2x886$ = 1772
1631				$2290+360$ = 1650
1466			$1474$	$\text{OH}_2$ Bending
1458			$1467$	$\text{CH}_3$ Asymmetric Bending
1455	1455		$1460$	
1435	1439		$1456$	
	1380		$1441$	$\text{CH}_3$ Asymmetric Bending
1363	1374		$1376$	$\text{CH}_3$ Symmetric Bending
	1367		$1370$	
	1354		$1364$	
			$1359$	$\text{CH}_2$ Wagging
			$1351$	
			$1282$	
1285	1289		$1294$	
	1242		$1288$	$\text{CH}_2$ Twisting
			$1279$	
1185			$1207$	$1014+(240) = 1254$
			$1200$	
			$1193$	$\text{CH}_3$ Rocking.
1112	1153		$1161$	$\text{CH}_3$ Rocking.
	1115		$1136$	$\text{COC}$ Asymmetric Stretch
			$1128$	
			$1023$	
			$1017$	$\text{CH}_2$ Rocking.
			$1009$	
	1014			
				$1360-(360) = 1000$
	990			$2256-1289 = 967$
	961			
	955			

TABLE I (Cont.)

LIQUID (Raman)	SOLUTIONS			VAPOUR	ASSIGNMENT
	Capillary 0.75mm.	CCl <sub>4</sub> (0.5cm.)	CS <sub>2</sub> (0.5cm.)		
914	915	919	917	937 922 924 399 890 832	CO-C Symmetric stretching
382	886	385	695		C-C Stretch
404	344 704 536 (425) (360) (230)	838 709 536		2x420 = 840 2x350 = 700 350+240 = 590	CO-C Bending CCO Bending CCN Bending
352					
242					

TABLE 2: INFRARED SPECTRUM OF METHYL CHLOROMETHYL ETHER.

Raman	LIQUID Capillary	O. 1mm.	SOLUTION		VAPOUR	ASSIGNMENT
			CCl <sub>4</sub>	CS <sub>2</sub>		
3037		4459			2295+1470 = 4465	
2990		4415			2958+1470 = 4428	
2950		4284			2903+1398 = 4300	
2912		4207			2905+1320 = 4223	
2837		4091			2837+1278 = 4115	
		4028			2837+1193 = 4030	
		3961			2837+1120 = 3957	
					Asymmetric Stretch	
					CH <sub>2</sub>	Syn. etric Stretch
					CH <sub>2</sub>	Asymmetric Stretch
					CH <sub>3</sub>	Asymmetric Stretch
					CH <sub>3</sub>	Symmetric Stretch.
					1460+1320 = 2780	
					2x1320 = 2640	
					1460+1156 = 2616	
					1470+996 = 2466	
					1320+1120 = 2440	
					2x1193 = 2386	
					1397+920 = 2317	
					1320+920 = 2240	
					1278+920 = 2198	
					1193+920 = 2113	
					920+1120 = 2040	
					2x920 = 1840	
					2903-1120 = 1783	
					1320+350 = 1650	
					2995-1397 = 1598	
					CH <sub>2</sub> Bending	
1470		1470			1476	
1467		1467			1470	
1460		1460			1458	Asymmetric Bending
					1451	CH <sub>3</sub> Asymmetric Bending

TABLE 2: (Cont.)

	LIQUID	SOLUTION	VAPOUR	ASSIGNMENT
Raman	Capillary 0.1	CCl <sub>4</sub>	CS <sub>2</sub>	
1435	1440	1446	1440)	
1398	1397	1396	+08 1400	CH <sub>3</sub> Symmetric Bending
			{ 1392	
1321	1320	1317	1331	
			{ 1324	CH <sub>2</sub> Wagging
1279	1273	1315	1317	
1231			{ 1286	CH <sub>2</sub> Twisting
			{ 1278	
			{ 1270	
			{ 1236	1397-160 = 1237
			{ 1206	
			{ 1198	CH <sub>3</sub> Rocking
			{ 1190	
1156		1153	1156	
1147		1138	1148	CH <sub>3</sub> Rocking
1128		1129	1138	
			{ 1128	COC Asymmetric Stretch
			{ 1121	
1043		1120	1092	1450-350 = 1100
998			1064	1397-350 = 1047
920	920	1043	1054	
		990	1008	CH <sub>2</sub> Rocking
			{ 993	
			{ 943	
		925	937	COC Symmetric Stretch
			{ 932	
		917		
				350+466 = 816
		805		

TABLE 2: (Cont.)

LIQUID		SOLUTION		VAPOUR	ASSIGNMENT
Raman	Capillary 0.1mm.	CCl <sub>4</sub>	CS <sub>2</sub>		
651	646		640	686 679 677 670	C=C1 Stretch
455	466				CC=C1 Bending
357	(350, (160)				CH <sub>3</sub> -C=O Torsion
177					CH <sub>3</sub> -O-C <sub>2</sub> Cl Torsion
107					

TABLE 3. DIMENSIONS OF CH<sub>3</sub>.O.CH<sub>2</sub>.X MOLECULES.

MOLECULE	C-O	CO-C	O-C-X	C-C(I)	C≡N(I)	C-Cl(II)
CH <sub>3</sub> .O.CH <sub>2</sub> .CN	1.42	110°	111°	1.47	1.16	-
CH <sub>3</sub> .O.CH <sub>2</sub> .Cl	1.42	110°	112°	-	-	1.74

TABLE 4. CALCULATED MOMENTS OF INERTIA AND ROTATIONAL CONSTANTS OF CH<sub>3</sub>.O.CH<sub>2</sub>.X MOLECULES.

(a) CH<sub>3</sub>.O.CH<sub>2</sub>.CN

Conformation	I <sub>A</sub>	A	I <sub>B</sub>	B	I <sub>C</sub>	C
I	53	0.53	166	0.17	219	0.13
II	41	0.68	224	0.13	270	0.10
III	28	0.99	157	0.18	175	0.16
IV	38	0.75	266	0.11	343	0.08
V	17	1.65	321	0.09	338	0.08

(b) CH<sub>3</sub>.O.CH<sub>2</sub>.Cl

Conformation	I <sub>A</sub>	A	I <sub>B</sub>	B	I <sub>C</sub>	C
I	63	0.45	161	0.17	224	0.13
II	51	0.55	205	0.14	244	0.12
III	23	1.20	147	0.19	161	0.18
IV	59	0.47	242	0.12	329	0.09
V	14	2.02	304	0.09	318	0.09

TABLE 5: CALCULATED P.R SEP RATIOS OF PARALLEL-TYPE BANDS ( $\Delta \gamma$ ).

(a)  $\text{CH}_3\text{OCH}_2\text{CN}$

CONFORMATIONS	I	II	III	IV	V
$\Delta \gamma$ (P,R) $\text{cm}^{-1}$	1.1	17.9	21.5	16.1	13.9

(b)  $\text{CH}_3\text{OCH}_2\text{Cl}$

CONFORMATIONS	I	II	III	IV	V
$\Delta \gamma$ (P,R) $\text{cm}^{-1}$	20.4	18.0	20.9	15.5	13.5

TABLE 6: OBSERVED P.R SEPARATIONS OF PARALLEL-TYPE BANDS.

$\text{CH}_3\text{OCH}_2\text{CN}$	$\text{CH}_3\text{OCH}_2\text{Cl}$
1349	1408
1359	1400
1364	1392
1279	1331
1283	1324
1294	1317
1193	1286
1200	1278
1207	1270
1123	1156
1128	1148
1136	1138
1009	1121
1017	1120
1023	1138
924	686
922	679
937	677
	670

TABLE 7: FREQUENCIES OF SKELETAL VIBRATIONS.

MOLECULE	b(COC)	b(OCC)	b(XCC)	Ref.
$\text{CH}_3\text{OCH}_3$	414	-	-	9
$\text{CH}_3\text{OCHO}$	325	-	-	10
$\text{CH}_3\text{O.CO.CH}_3$	303	429	-	10
$\text{CH}_3\text{CH}_2\text{OH}$	-	427	-	13
$\text{CNCH}_2\text{CN}$	-	-	582	14
$\text{CH}_3\text{CH}_2\text{CN}$	-	-	531	15
$\text{CH}_3\text{CH}_2\text{F}$	-	-	415	16
$\text{HOCH}_2\text{CN}$	-	410	-	17

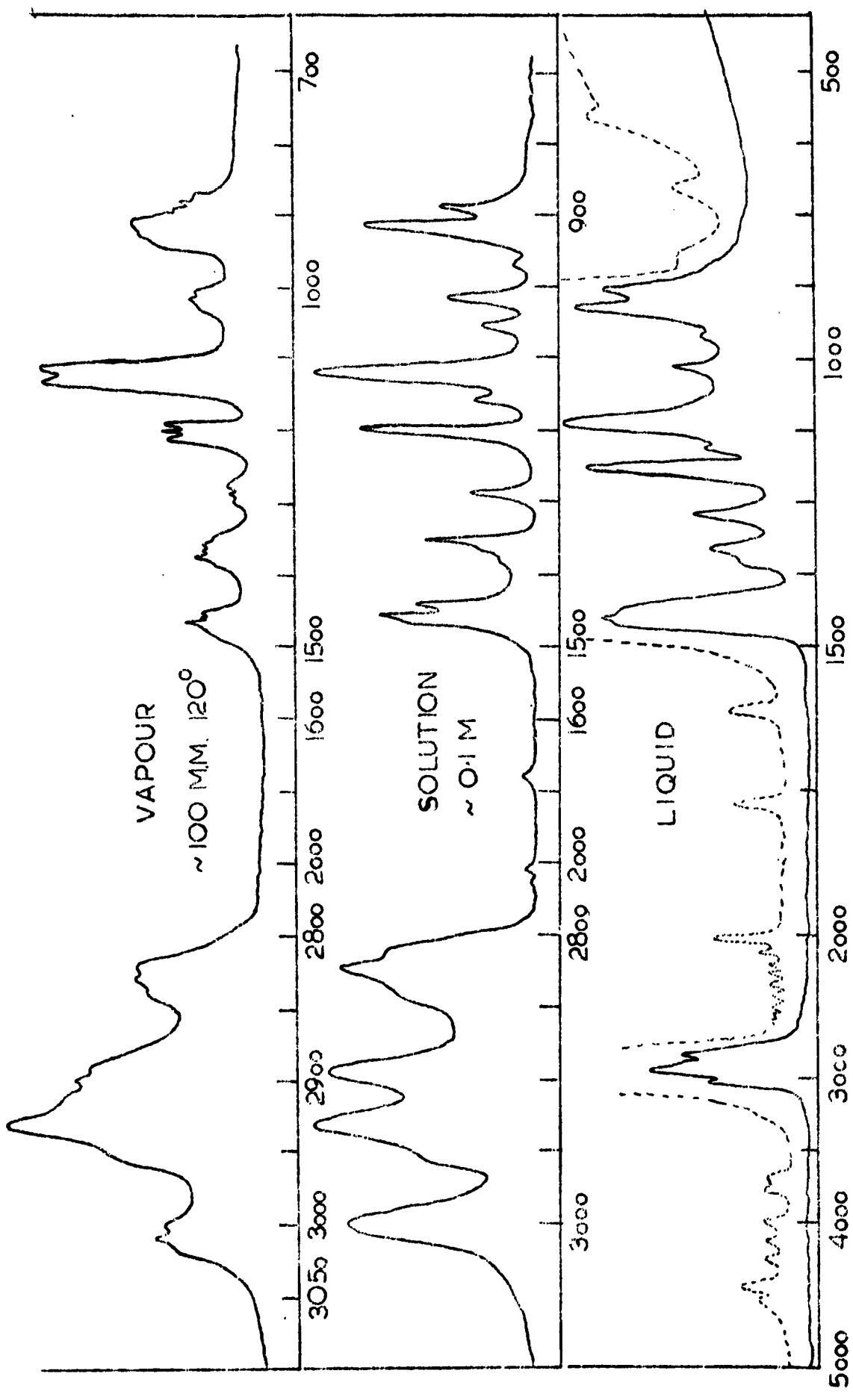


FIG. I  
 $\text{CH}_3\text{OCH}_2\text{CN}$

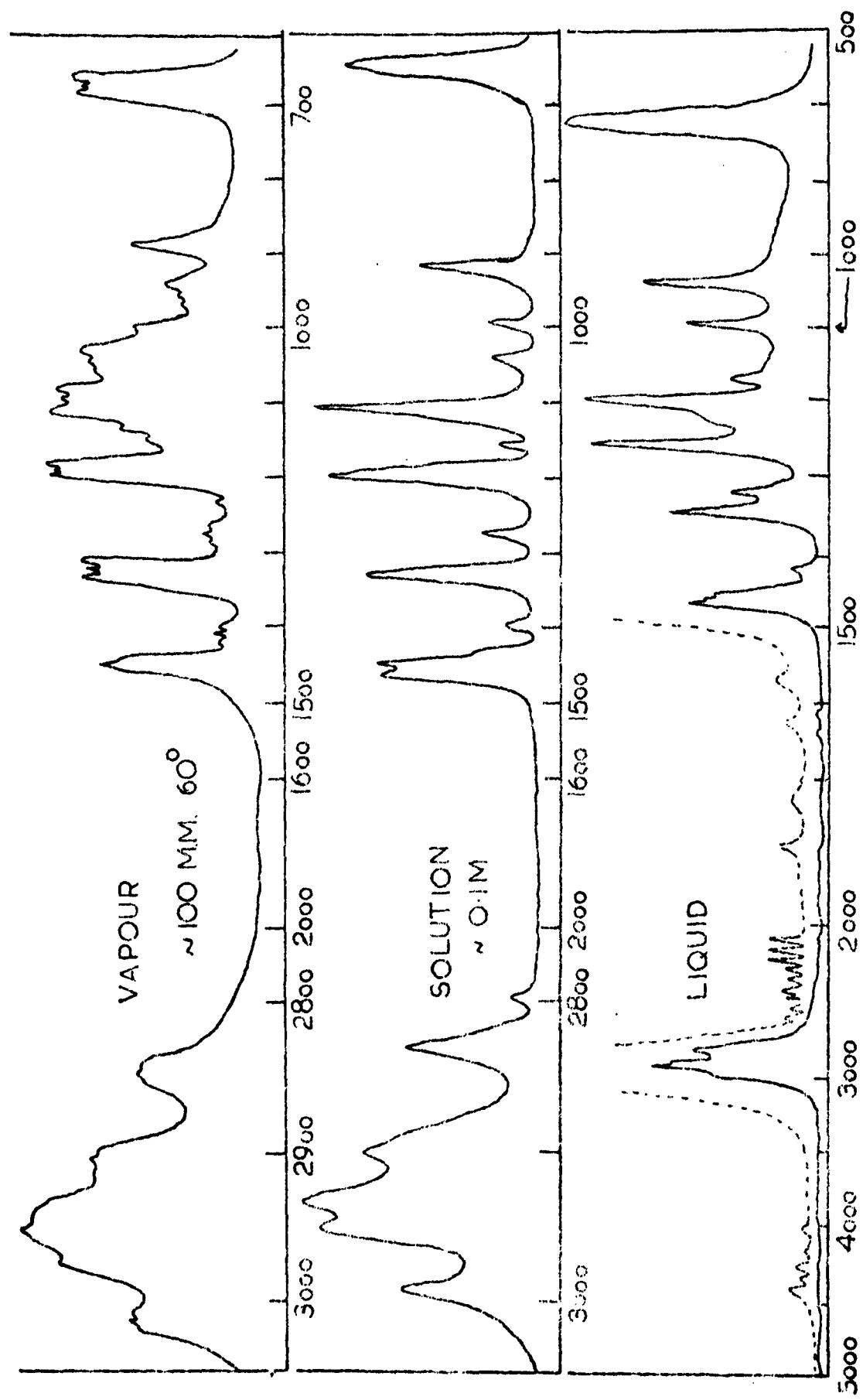


FIG 2  $\text{CH}_3\text{OCH}_2\text{Cl}$

FIG. 3 CONFORMATIONS OF  $\text{CH}_3\text{OCH}_2\text{X}$  MOLECULES.

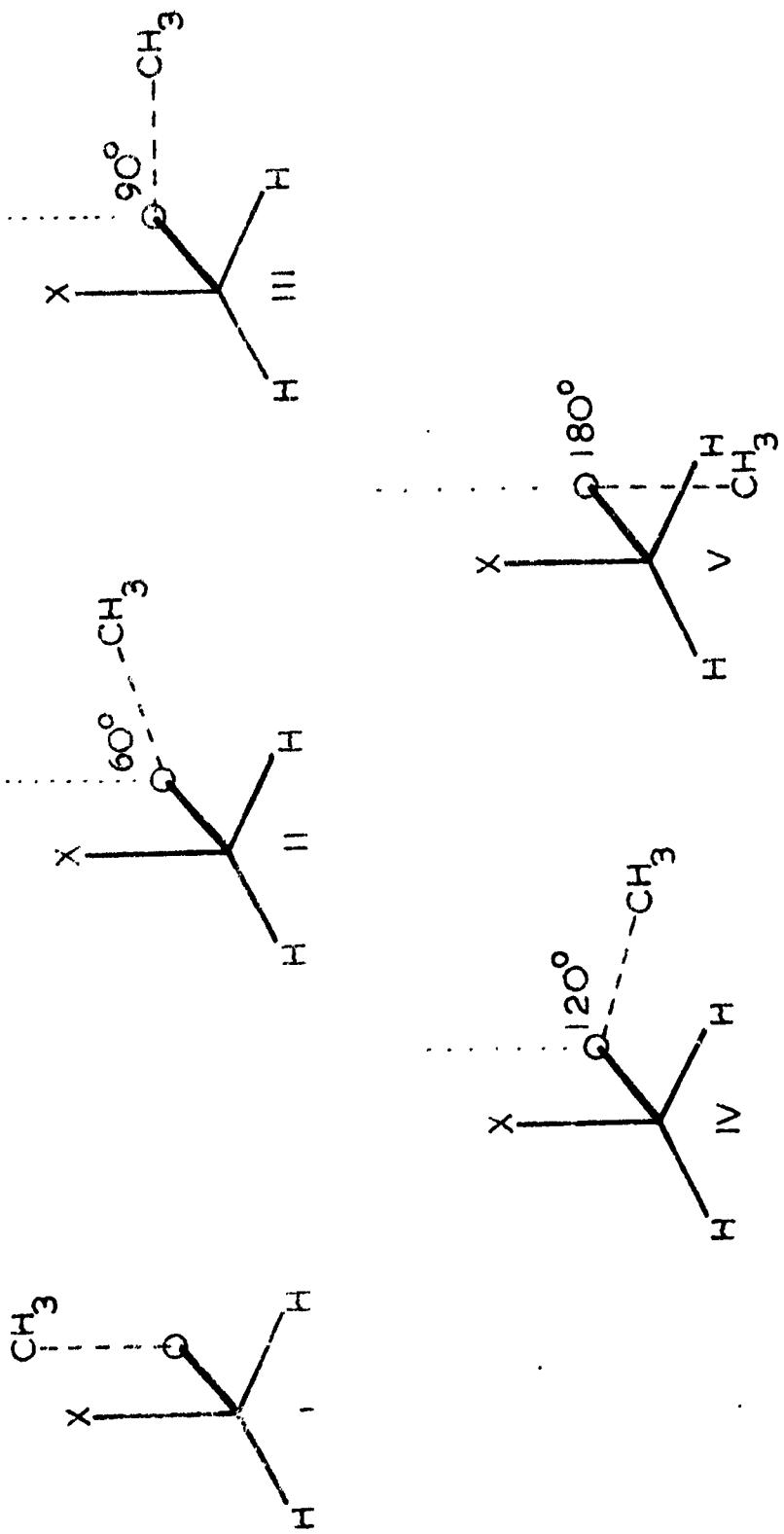


FIG. 4A

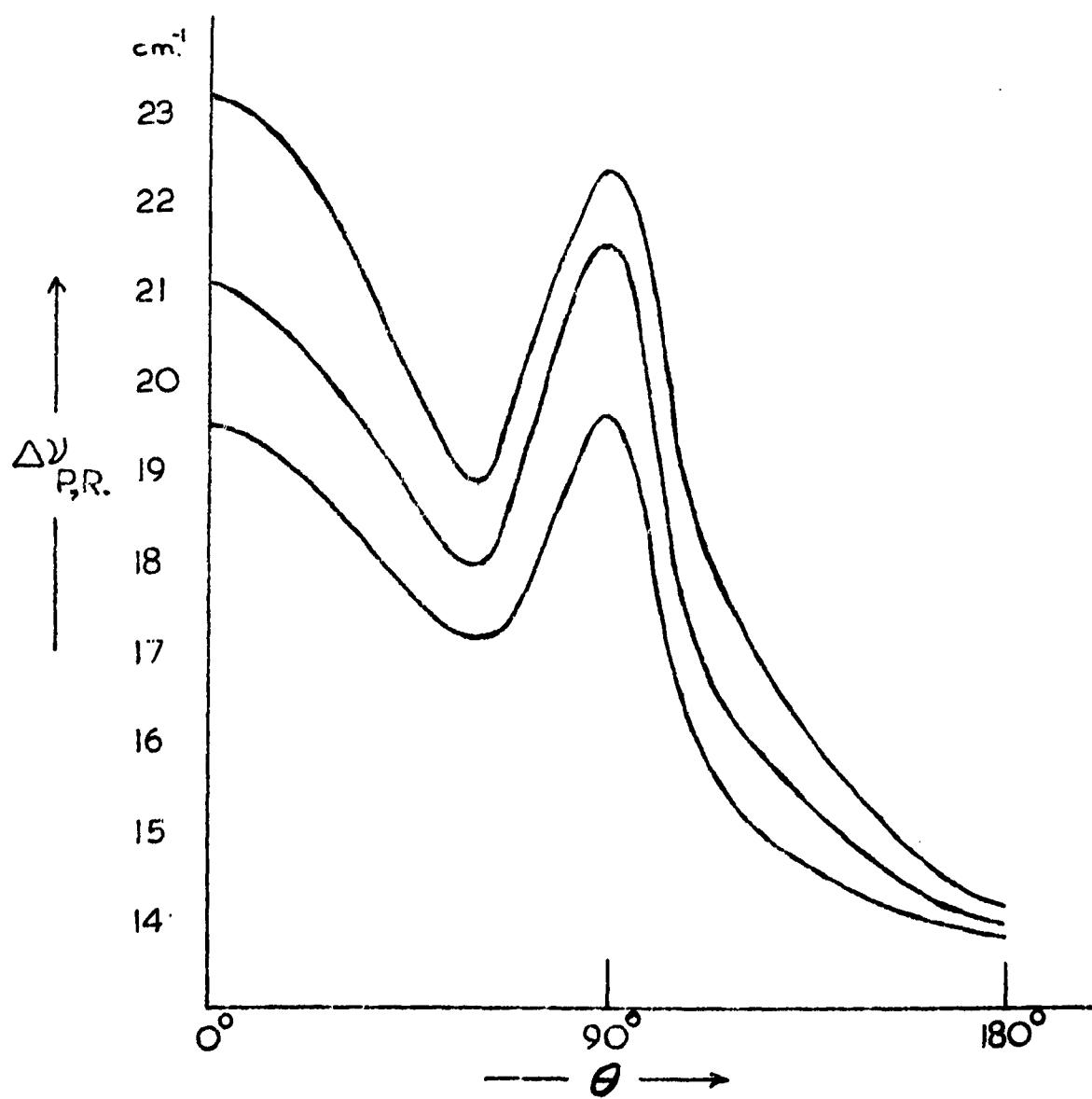
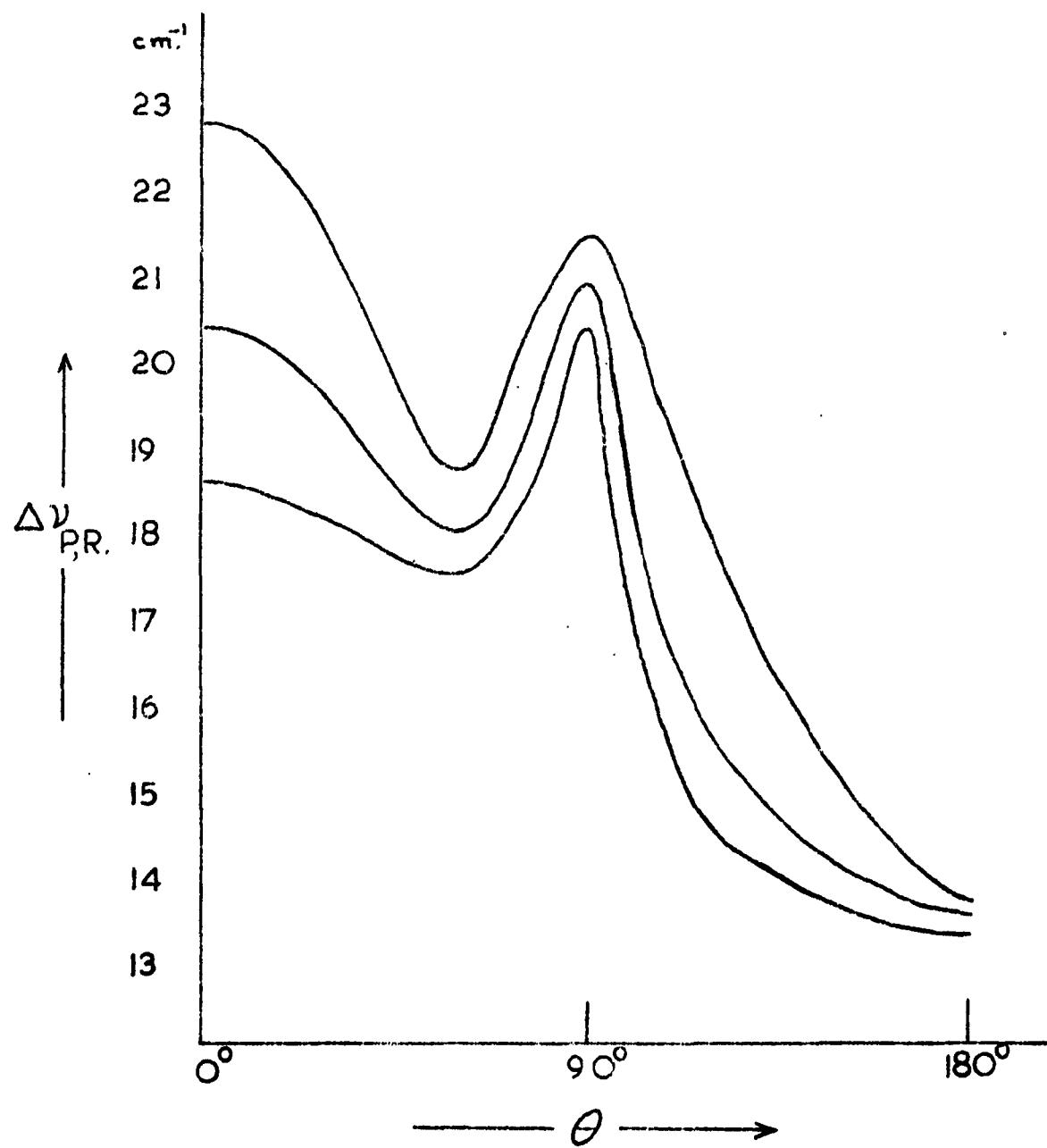
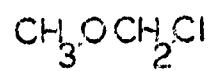


FIG 4B



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